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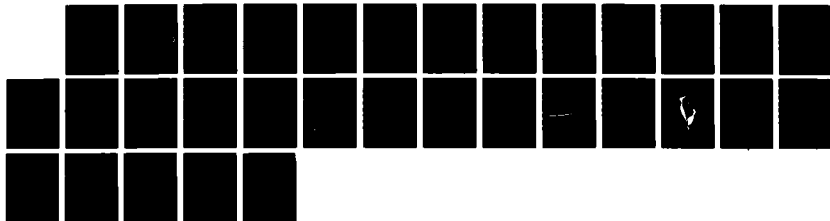
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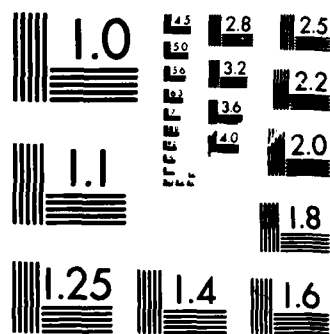
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SYNTHESIS OF CONJUGATED POLYMERS VIA POLYMER ELIMINATION

by

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SYNTHESIS OF CONJUGATED POLYMERS
VIA POLYMER ELIMINATION REACTIONS

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The transformation of nonconjugated polymers into conjugated polymers using elimination reactions is described. Heterocyclic conjugated polymers containing alternating aromatic and quinonoid sections in the main chain are synthesized by chemical or electrochemical redox elimination reaction on soluble precursor polymers containing sp^3 -carbon atom bridges between the aromatic heterocyclic units. Progress of the redox elimination process is followed by infrared and electronic spectra as well as by cyclic voltammetry. A reaction mechanism in which the precursor polymer undergoes a redox reaction followed by loss of the bridge hydrogens is proposed. The resulting conjugated aromatic/quinonoid polymers generally have very small semiconductor band gaps in accord with predictions of recent theoretical calculations. A brief review of related syntheses of conjugated polymers from nonconjugated precursor polymers is also given.

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Conjugated polymers are currently of wide interest because of their electronic (1), electrochemical (2), and nonlinear optical (3) properties which originate from their delocalized π -electron systems. Unfortunately, the high density and geometrical disposition of π -bonds in conjugated polymers which confine the desirable electronic and optical properties also make them more insoluble and infusible relative to nonconjugated polymers. The many synthetic routes to conjugated polymers may be classified into two broad categories: (1) those in which the target conjugated polymer is obtained directly from conventional addition and condensation polymerization processes (4), and (2) those involving transformation of an existing nonconjugated precursor polymer into the target conjugated polymer (5). The latter approach is especially attractive since the nonconjugated precursor polymer can be more readily processed into films and other forms prior to conversion to the

conjugated derivative. Also, the nonconjugated precursor polymer route will allow the tuning of physical properties of the conjugated derivative, including density, morphology, crystallinity, and electronic and optical properties. Among the possible polymer reactions which could be used to convert nonconjugated polymers into conjugated ones are elimination, addition, and isomerization (5), but our primary interest here is polymer elimination reactions.

One of the earliest known synthesis of a conjugated polymer by elimination on a nonconjugated precursor was achieved by Marvel *et al* (6) who demonstrated that polyacetylene was obtained by elimination of HCl from polyvinyl chloride as illustrated in Figure 1. Feast and his co-workers have recently described an elegant synthesis of polyacetylene (PA) films by thermal elimination of aromatic hydrocarbons such as 1,2-bis(trifluoromethyl)benzene, naphthalene and anthracene from films of soluble nonconjugated precursor polymers (7), Figure 2. The resulting polyacetylene films, now known in the literature as Durham polyacetylene, have physical properties that are significantly different from the Shirakawa polyacetylene: Durham PA is largely amorphous and has a non-fibrous morphology compared to Shirakawa PA which is highly crystalline and fibrous (8-9). Also recently, Lenz, Karasz and co-workers (10) have reported the synthesis of poly(p-phenylenevinylene) (PPV) films by thermal elimination of $(CH_3)_2S$ and HCl from poly(p-xylylene- α -dimethyl-sulfonium chloride), a soluble polyelectrolyte (see Figure 3). Highly oriented Durham PA and PPV films with stretch ratios up to 20 have been obtained by stretching the precursor polymer films during the transformation to conjugated derivatives; such oriented films when doped give rise to conductors with large anisotropy in electrical conductivity. The Durham route to polyacetylene and the above PPV synthesis demonstrate the rich potentials of synthesis of conjugated polymers via elimination reactions on nonconjugated precursor polymers.

Recently, we discovered a novel type of polymer elimination reaction for producing conjugated polymers from the class of nonconjugated polymers containing alternating sp^3 -carbon atom ($-C(R)H-$) and conjugated sections in the main chain (11-13). Under chemical or electrochemical oxidative or reductive conditions such polymers undergo irreversible reactions leading to loss of the bridge hydrogens, converting the sp^3 -carbon to sp^2 -carbon as illustrated in Figure 4, where D or A denotes π -electron donor or acceptor conjugated sections. Initial observations on this redox elimination reaction were made on poly(3,6-N-methylcarbazolediyl methylene) (PMCZM) (11) and poly(3,6-N-methylcarbazolediyl benzylidene) (PMCZB) (12). For example, upon oxidation of PMCZM and PMCZB with bromine or iodine it was shown that a bridge hydrogen was eliminated as HBr or HI resulting in fully conjugated doped derivatives which had dc conductivities (0.1-1 S/cm) as high as the parent poly(3,6-N-methylcarbazolediyl) (11-12). Figure 5 shows the optical absorption spectra of a film of PMCZM before and after a prolonged exposure to iodine vapor. The large red shift, corresponding to a narrowing of the optical band gap or increase in the degree of conjugation is to be noted. Also, it is significant that elimination of the bridge hydrogens ($-C(R)H-$) in PMCZM and PMCZB produced conjugated polymers containing quinonoid sections in the main chain. These initial

observations lead us to pursue the synthesis of conjugated polymers containing alternating aromatic and quinonoid sequences in the main chain via redox elimination on precursors, such as the heterocyclic conjugated polymers of Figure 6. Extensive recent theoretical calculations predict that very narrow band gaps would be obtained in conjugated polymers containing quinonoid sections (14-18). We recently reported the smallest bandgap in organic polymers for such conjugated polymers (19).

In this paper we present results on the polymer redox elimination reaction used in the synthesis of the polymers in Figure 6. Preliminary results on electrochemical redox elimination on precursor polymers are also presented. A mechanism of the polymer elimination reaction is proposed. Related recent experimental observations at other laboratories that can be described within the framework of the scheme of Figure 4 are discussed.

Experimental

Precursor Polymers. The synthesis and characterization of the nonconjugated precursor polymers containing alternating heteroaromatic units and $-C(R)H-$ in the main chain are described elsewhere (20-21). These nonconjugated precursor polymers include polythiophenes, polypyrroles and polyfurans; however, only the studies done with some of the polythiophenes and their related conjugated derivatives are described in detail here: poly(2,5-thiophenediyl benzylidene) (PTB), poly[α -(5,5'-bithiophenediyl) benzylidene] (PBIB), poly[α -(5-5'-bithiophenediyl)p-acetoxylbenzylidene] (PBAB), and poly[α -(5-5''-terthiophenediyl) benzylidene] (PTTB). These precursor polymers are soluble in organic solvents including tetrahydrofuran (THF), methylene chloride and N,N-dimethylformamide (DMF). Thin films used in spectroscopy and for cyclic voltammetry were cast from THF, methylene chloride or DMF.

Elimination Procedures. Chemical redox-induced elimination was performed on precursor thin films by exposure to bromine or iodine vapor or by immersion of films in hexane solutions of these halides.

In order to follow progress of elimination, reactions were also performed on thin films in a special sealed glass cell which permitted *in situ* monitoring of the electronic or infrared spectra at room temperature (23°C). Typically, the infrared or electronic spectrum of the pristine precursor polymer film was obtained and then bromide vapor was introduced into the reaction vessel. *In situ* FTIR spectra in the 250-4000 cm^{-1} region were recorded every 90 sec with a Digilab Model FTS-14 spectrometer and optical absorption spectra in the 185-3200 nm (0.39-6.70 eV) range were recorded every 15 min with a Perkin-Elmer Model Lambda 9 UV-vis-NIR spectrophotometer. The reactions were continued until no visible changes were detected in the spectra.

Cyclic voltammetry was performed on precursor polymer thin films cast on platinum electrodes in order to assess the possibility of electrochemical redox elimination and consequently as an alternative means of monitoring the process. All electrochemical experiments were performed in a three-electrode, single-compartment cell using a double junction $\text{Ag}/\text{Ag}^+(\text{AgNO}_3)$ reference electrode in 0.1M

tetraethylammonium perchlorate (TEAP)/acetonitrile. The voltage regulator was a Princeton Applied Research Model 175 Universal programmer. Current measurement was done using a Princeton Applied Research Model 173 Potentiostat/Galvanostat in conjunction with Princeton Applied Research Model 376 logarithmic current converter. The cyclic voltammograms were recorded on a HP Model 7040A X-Y recorder.

Results

Figure 7 shows the FTIR spectra of initial precursor PBTB film (A) and at two subsequent times (B and C) during in situ elimination reaction with bromine vapor at 23°C. Several main changes in the infrared spectrum of the precursor film are observed. The aliphatic C-H stretching vibration bands in the 2800-3000 cm^{-1} region attributed to the bridge sp^3 C-H are significantly modified, generally decreasing with elimination reaction time and eventually disappearing. In contrast, the absorption bands in the 3060-3250 cm^{-1} region attributed to the side chain phenyl and thiophene C-Hs remain relatively the same. A new gas phase absorption band at 2400-2800 cm^{-1} assigned to evolved HBr gas appears as seen in Figure 7 (B and C). The gas phase absorption band attributed to HBr gas appeared in the first spectrum after bromine was introduced into the reaction cell and intensified with reaction time. New absorption bands appeared and intensity of existing ones increased in the carbon-carbon double bond absorption region, 1000-1600 cm^{-1} . There was no evidence of a new band in the 500-650 cm^{-1} region that would be attributable to a C-Br bond due to substitution or bromination reactions on the polymer chain. These IR spectra results clearly show that the bridge hydrogens ($-\text{C}(\text{R})\text{H}-$) of PBTB are eliminated as HBr by reaction with bromine, yielding the anticipated aromatic/quinonoid conjugated polymers of Figure 6.

The electronic absorption spectra at different times of elimination reaction on PBTB are shown in Figure 8. As-synthesized PBTB is a green polymer (Curve 1, Figure 8) due to partial conversion of the $-\text{C}(\text{R})\text{H}-$ to $-\text{C}(\text{R})=$ bridges in the main chain (19-21). After 15 min. reaction time, the electronic spectrum is greatly red-shifted with the absorption edge now located at about 1200 nm (1.03 eV). Progress in elimination further moves the absorption edge to longer wavelength as curves 2 to 13 in Figure 8 show. No observable changes in the electronic absorption spectra were seen after 24 hours (Curve 13). Visually, the sample changes from green (Curve 1) to metallic gray in color. The absorption edge determined from Curve 13 is about 1500 nm (0.83 eV). This represents an extremely large increase in the degree of π -electron delocalization. The relatively sharp absorption edges are also noteworthy.

Figure 9 shows the electronic absorption spectrum of a PTTB film which has undergone extensive but incomplete reaction with bromine in a non-in-situ experiment. The absorption spectrum is that expected for a one-dimensional conjugated polymer. The sharpest absorption edge is at about 1490 nm (0.83 eV) and the absorption maximum is located at 1240 nm (1.0 eV). Thus, this material has a bandgap of about 0.83 eV. Note that two small

absorptions can be seen below the gap at 1560 nm (0.79 eV) and 1950 nm (0.64 eV). The two absorptions below the bandgap may be interpreted as evidence of charged bipolarons (dications) (22). However, no such below bandgap absorptions are observed in the completely reacted material.

Some of the results of cyclic voltammetric studies of a film of PBTAB at various stages of redox elimination are shown in Figures 10A and 10B. The cyclic voltammogram of Figure 10A shows the behavior of a precursor PBTAB film on platinum electrode under repeated cycling at 200mV/s. Initially, an oxidation peak at about 0 V (vs. Ag/Ag⁺), a main reduction peak at -0.56 V and a small broad reduction peak centered at -0.15 V are observed. This initial voltammogram is very unstable under cycling: (i) the redox peaks at -0.56 V and 0.0 V are decreasing; and (ii) evolving very broad peaks that form a redox couple are observed in the range +0.14-0.21 and -0.09 to -0.23 V. After numerous cycling (~100) over a period of hours the resulting polymer film was washed and its cyclic voltammogram was again obtained in a fresh electrolyte. A reversible redox couple with oxidation peak at +0.21 V and reduction peak at -0.24 V was obtained as shown in Figure 10B. This later cyclic voltammogram is quite stable under repeated cycling and is what one might expect for an electroactive conjugated polymer. These results suggest that the electrochemical redox reaction induces elimination of the -C(R)H- bridge hydrogens, yielding -C(R)= bridges.

Preliminary measurements of electrical conductivity of the conjugated derivatives of PBTAB, PBTB and PTTB obtained by the above treatment with bromine vapor are poor semiconductors with a conductivity of the order 10⁻⁶S/cm which apparently is not due to doping. Subsequent electrochemical or chemical doping of these polymers lead to 4-6 orders of magnitude increase in conductivity. Ongoing studies of the electrical properties of these conjugated polymers with alternating aromatic/quinonoid units will be reported elsewhere.

Similar redox elimination reactions have been performed on several heteroaromatic precursor polymers within the class shown in Figure 4 and whose conjugated derivatives are shown in Figure 6. In general, the results and observations are similar to those described here. The major differences observed are due to differences in the heteroatom (X) while minor differences are observed with different R groups. For example, the smallest bandgaps were obtained when X=S in the polymers of Figure 6. On the other hand, faster elimination kinetics were observed for aromatic R compared to aliphatic R side groups.

Discussion

The electronic absorption spectra of Figures 8 and 9, and those not shown, reveal that the conjugated polymers of Figure 6 generally exhibit intrinsic semiconductor bandgaps that are very small. This is in accord with extensive recent theoretical calculations which predict that introduction of quinoidal geometry into the main chain of aromatic conjugated polymers (e.g. polythiophene, polypyrrole, and poly-p-phenylene) reduces the bandgap. Especially relevant are the

valence effective hamiltonian (VEH) calculations of Bredas and co-workers (14-16) which are known to be very accurate in reproducing experimental data for conjugated polymers. In particular, Bredas has shown that as quinonoid structure is introduced into poly(2,5-thiophene) geometry the bandgap decreases linearly with increasing quinonoid character (14). More recently, the electronic band structures of the aromatic/quinonoid polymers of Figure 6 have been obtained using MNDO polymer geometry optimized total energy calculations (23). The theoretical energy bandgaps (23) were found to be in agreement with the experimental results (19).

Mechanism of Redox Elimination. The proposed elimination reaction mechanism is illustrated with a methylene-bridged polybithiophene in Figure 11. If one considers attempts to oxidize the nonconjugated precursor polymer by electron withdrawal or reduce it by electron addition, one finds that the added charge cannot be accommodated by delocalization because of the sp^3 hybridized carbon ($-CH_2-$) bridges. Consequently, highly unstable charged polymeric chains are generated. Depending on the sign of charge added to the precursor chain, such a high energy unstable intermediate would be best stabilized by loss of H^+ or H^- from adjacent bridges, yielding the neutral conjugated polymer chain containing alternating aromatic and quinoidal units. This mechanism can be used to explain the electrochemical results. For example, the observed decreasing redox peaks in the cyclic voltammogram of Figure 10A is attributed to the consumption of the charged intermediates. The optical absorption data of Figure 9 also appear to evidence bipolarons (dications) as intermediate and hence, consistent with this mechanism.

The general scheme of Figure 11 is for both electrochemical and chemical redox elimination. If we consider the case of oxidative elimination with bromine, generation of the necessary radical cation or dication intermediate is due to: $Br_2 + 2e^- \longrightarrow 2Br^-$. The bromide ions presumably then abstract protons from the ionized precursor.

Related Polymer Systems and Synthetic Methods. Figure 12A shows a hypothetical synthesis of poly (p-phenylene methide) (PPM) from polybenzyl by redox-induced elimination. In principle, it should be possible to accomplish this experimentally under similar chemical and electrochemical redox conditions as those used here for the related polythiophenes. The electronic properties of PPM have recently been theoretically calculated by Boudreaux et al (16), including: bandgap (1.17 eV); bandwidth (0.44 eV); ionization potential (4.2 eV); electron affinity (3.03 eV); oxidation potential (-0.20 vs SCE); reduction potential (-1.37 eV vs SCE). PPM has recently been synthesized and doped to a semiconductor (24).

The two limiting structural forms of polyaniline are shown in Figure 12B: (i) the nonconjugated leuco base polymer in which the imine nitrogens are completely protonated (PAN-1); and (ii) the neutral conjugated polymer containing alternating aromatic and quinoidal units (PAN-2). The highly conducting (10 S/cm) polyaniline chemically or electrochemically synthesized from aniline is believed to be a partially oxidized form with a structure intermediated between PAN-1 and PAN-2 (25-28). The complicated electrochemical behavior of polyaniline, especially in aqueous media, is a result of redox reactions coupled with reversible deprotonation/

protonation reaction. This polymer system with reversible conversion between PAN-1 and PAN-2 is to be contrasted with the irreversible polymer systems of Figures 4 and 12A. Theoretical calculations (28) of the electronic properties of both PAN-1 and PAN-2 show the best properties when the dihedral angle between adjacent rings on the chain is zero; PAN-1: bandgap (3.6 eV), bandwidth (3.0 eV), ionization potential (4.2 eV), oxidation potential (-0.2 V vs SCE), reduction potential (-3.8 V vs SCE); PAN-2: bandgap (0.7 eV), bandwidth (1.5 eV), ionization potential (5.3 eV), oxidation potential (+0.9 vs SCE), reduction potential (-0.2 V vs SCE). It is noteworthy that PAN-2 has a dramatically smaller bandgap than PAN-1.

Figure 13 shows the irreversible conversion of a nonconjugated poly (p-phenylene pentadienylene) to a lithium-doped conjugated derivative which has a semiconducting level of conductivity (0.1 to 1.0 S/cm) (29). Obviously, the neutral conjugated derivative of poly (p-phenylene pentadienylene) can then be reversibly generated from the n-type doped material by electrochemical undoping or by p-type compensation. A very similar synthetic method for the conversion of poly(acetylene-co-1,3-butadiene) to polyacetylene has been reported (30), Figure 14. This synthesis of polyacetylene from a nonconjugated precursor polymer containing isolated CH₂ units in an otherwise conjugated chain is to be contrasted with the early approach of Marvel *et al* (6) in which an all-sp³ carbon chain was employed.

Conclusions

Heterocyclic conjugated polymers containing alternating aromatic and quinonoid sections in the main chain have been synthesized by chemical or electrochemical redox elimination reaction on soluble precursor polymers containing -C(R)H- bridges between aromatic heterocyclic units. Progress of the redox elimination reaction converting the nonconjugated precursors to the conjugated polymers was monitored by infrared spectra, electronic absorption spectra and cyclic voltammetry. Some of the resultant conjugated polymers have the smallest known bandgaps among organic polymers (19) and the generally small semiconductor bandgaps are in accord with predictions of recent theoretical calculations (14-18, 23).

A reaction mechanism for the elimination reaction in which the precursor polymer undergoes redox reaction followed by loss of the bridge hydrogens is proposed. A brief review of related syntheses of conjugated polymers via elimination reactions on nonconjugated precursor polymers is given. It is suggested that this synthetic approach to conjugated polymers holds promise not only for achieving processing advantages but also for tuning electronic, optical and other physical properties of the target conjugated polymer.

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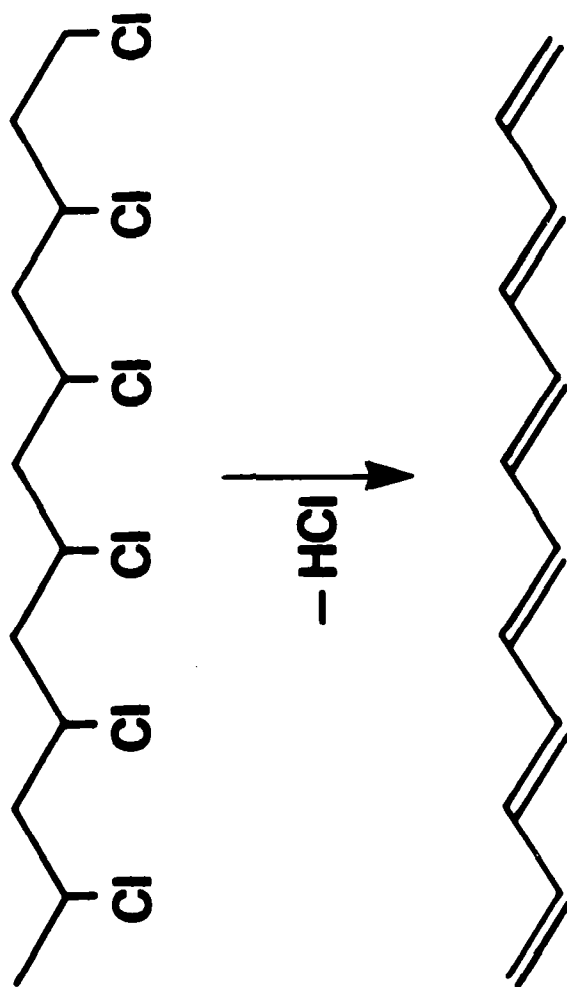
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- Figure 1. Synthesis of polyacetylene from polyvinyl chloride by elimination of HCl.
- Figure 2. The soluble nonconjugated precursor polymer route to Durham polyacetylene via thermal elimination.
- Figure 3. Synthesis of poly(p-phenylene vinylene) films by thermal elimination on a soluble polyelectrolyte.
- Figure 4. General scheme of irreversible redox elimination reaction on the class of nonconjugated polymers containing alternating $-C(R)H-$ and conjugated sections in the main chain yielding conjugated polymers.
- Figure 5. Optical absorption spectra of a thin film of precursor PMCZM (1) and after exposure to iodine vapor (2). Also shown is the proposed scheme of redox elimination yielding a doped conjugated conducting polymer.
- Figure 6. Novel conjugated heteroaromatic polymers synthesized by redox elimination.
- Figure 7. FTIR absorption spectra of precursor PBTB thin film (A) and during in-situ elimination (B and C) in bromine vapor at 23°C. Arrow indicates a superposed gas phase absorption band due to evolved HBr gas.
- Figure 8. Electronic absorption spectra of precursor PBTB thin film (1) and conjugated derivatives (2-13) at different times during in-situ elimination reaction at 23°C.
- Figure 9. Electronic absorption spectra of a conjugated derivative of PTTB.
- Figure 10A. Cyclic voltammogram of a precursor PBTAB thin film on Pt electrode in TEAP/acetonitrile at a scan rate of 200 mV/s.
- Figure 10B. Cyclic voltammogram of the same film in Figure 10A obtained after washing and running in a fresh TEAP/acetonitrile at a scan rate of 200 mV/s.
- Figure 11. Illustration of the proposed mechanism of redox-induced elimination.

- Figure 12. A possible synthesis of poly(p-phenylene methine) from polybenzyl via redox elimination (A). The two limiting structures of polyaniline (B).
- Figure 13. Synthesis of a conjugated derivative from poly(p-phenylene pentadienylene).
- Figure 14. Synthesis of polyacetylene from poly(acetylene-co-1,3-butadiene).



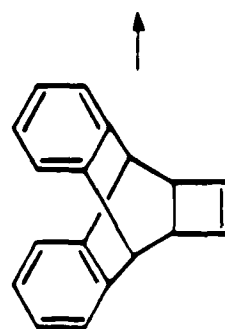
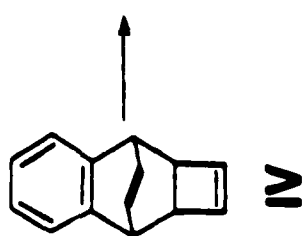
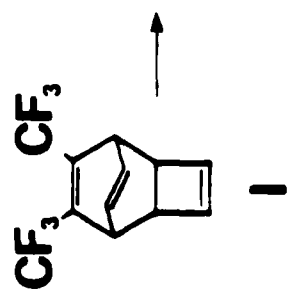
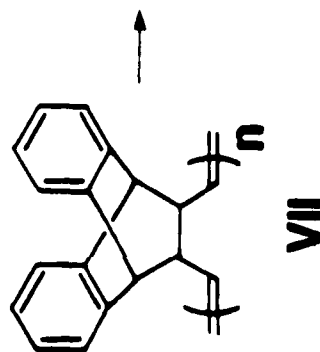
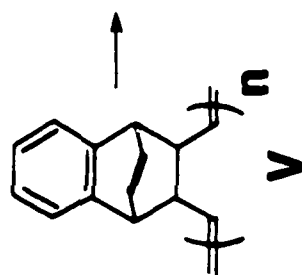
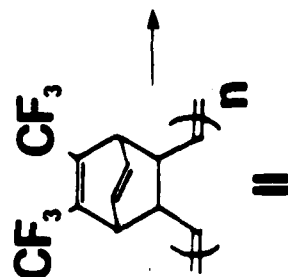
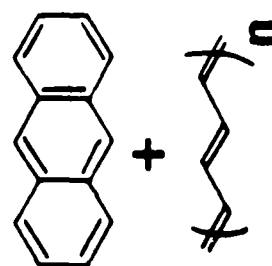
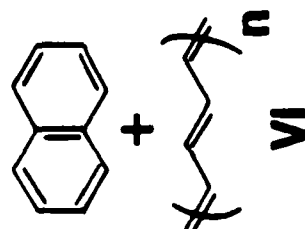
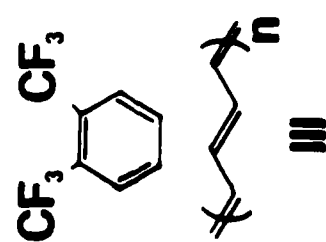
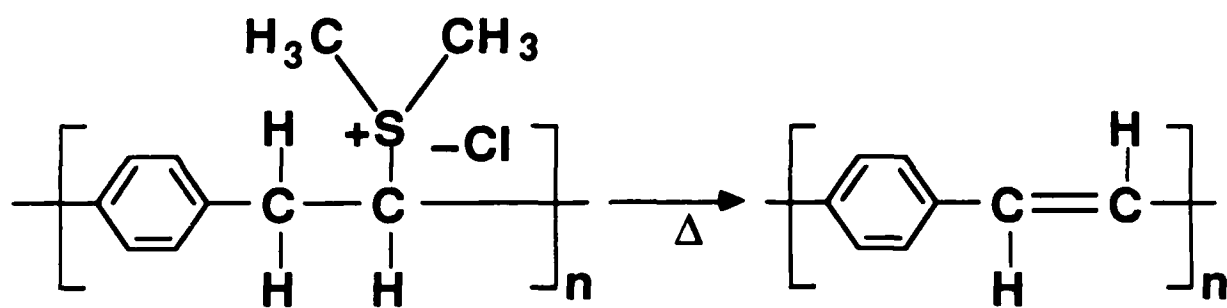
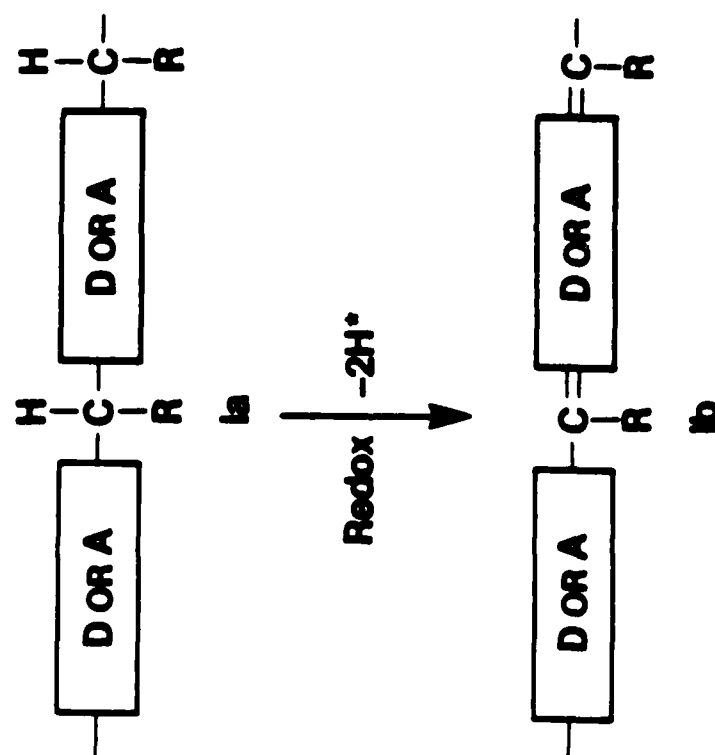


Fig. 3



SCHEME 1



SCHEME 2

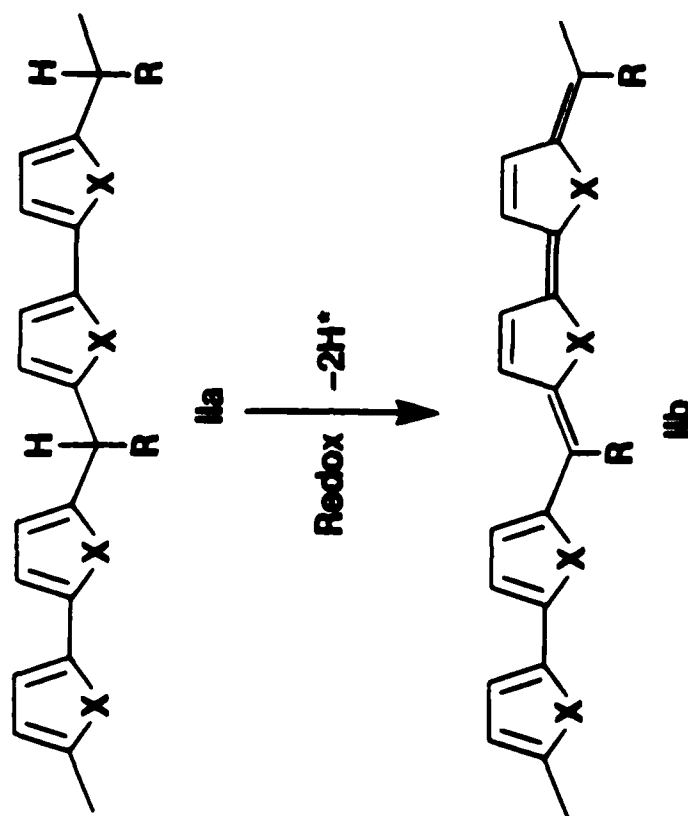
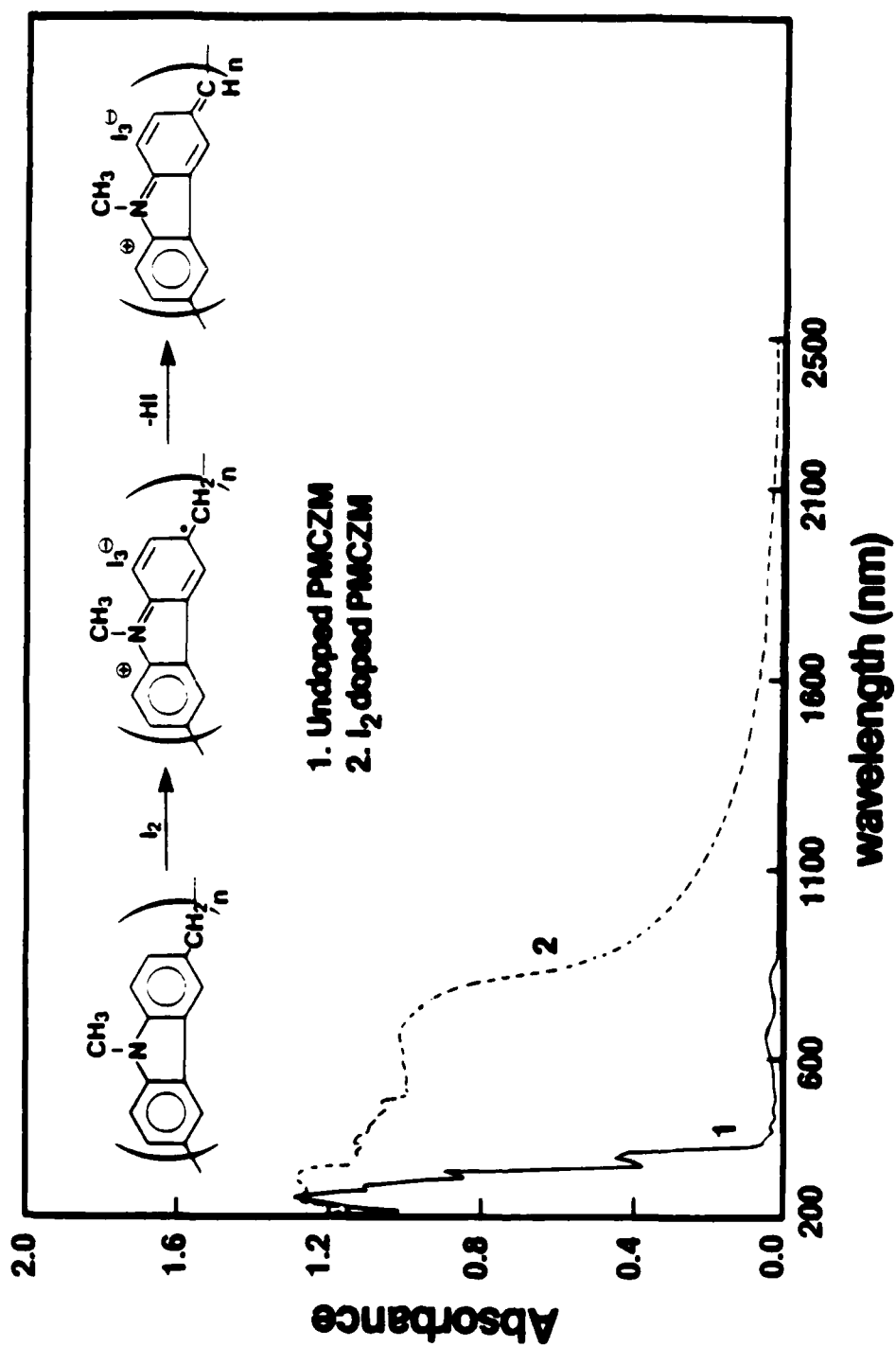


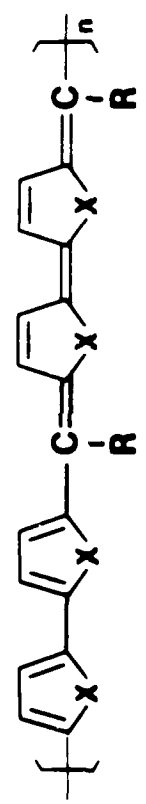
Fig. 5



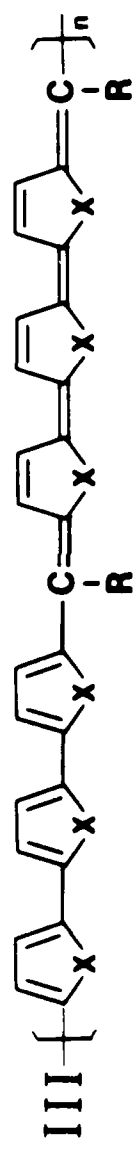
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I



II



III

Fig. 7

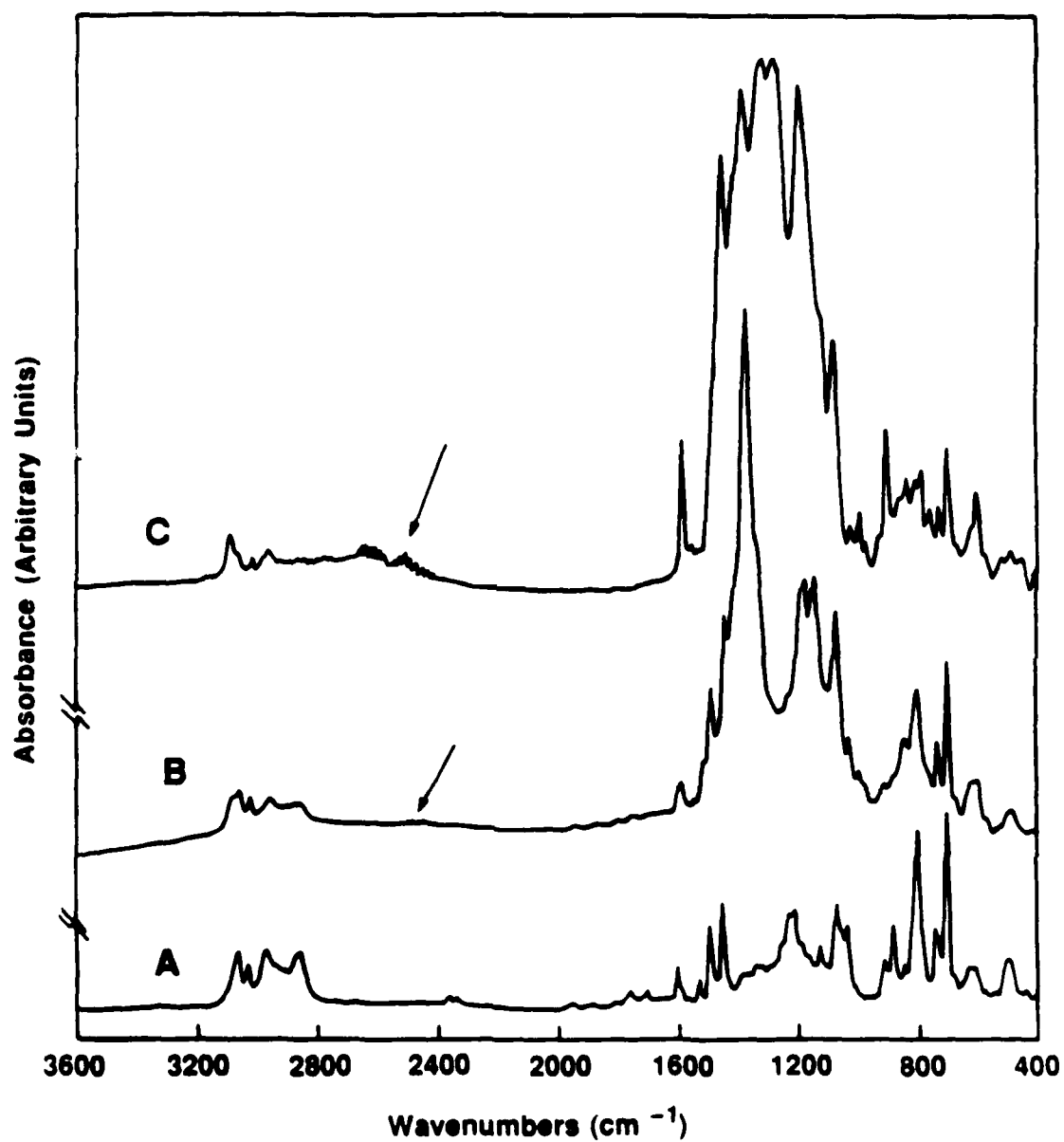


Fig. 8

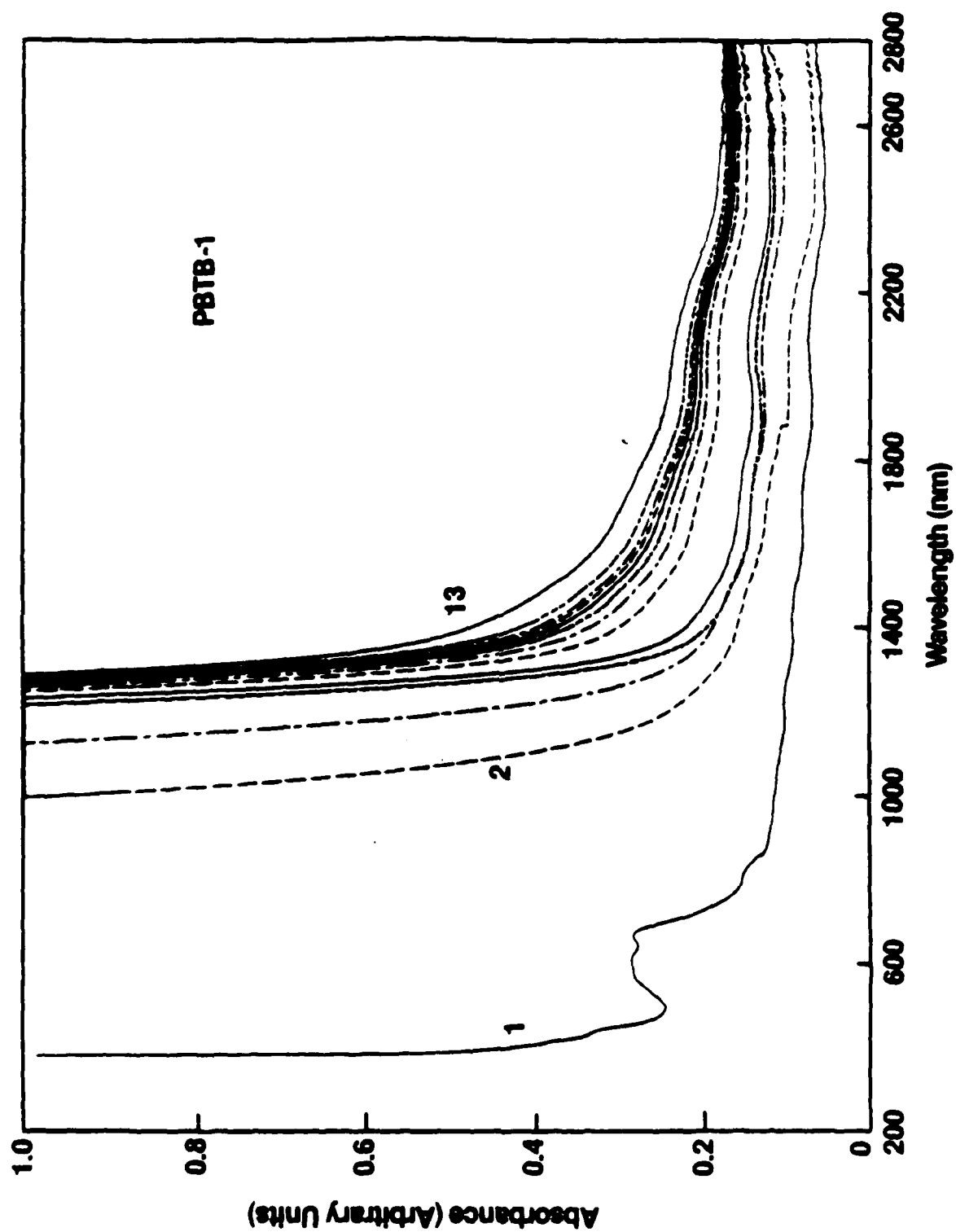
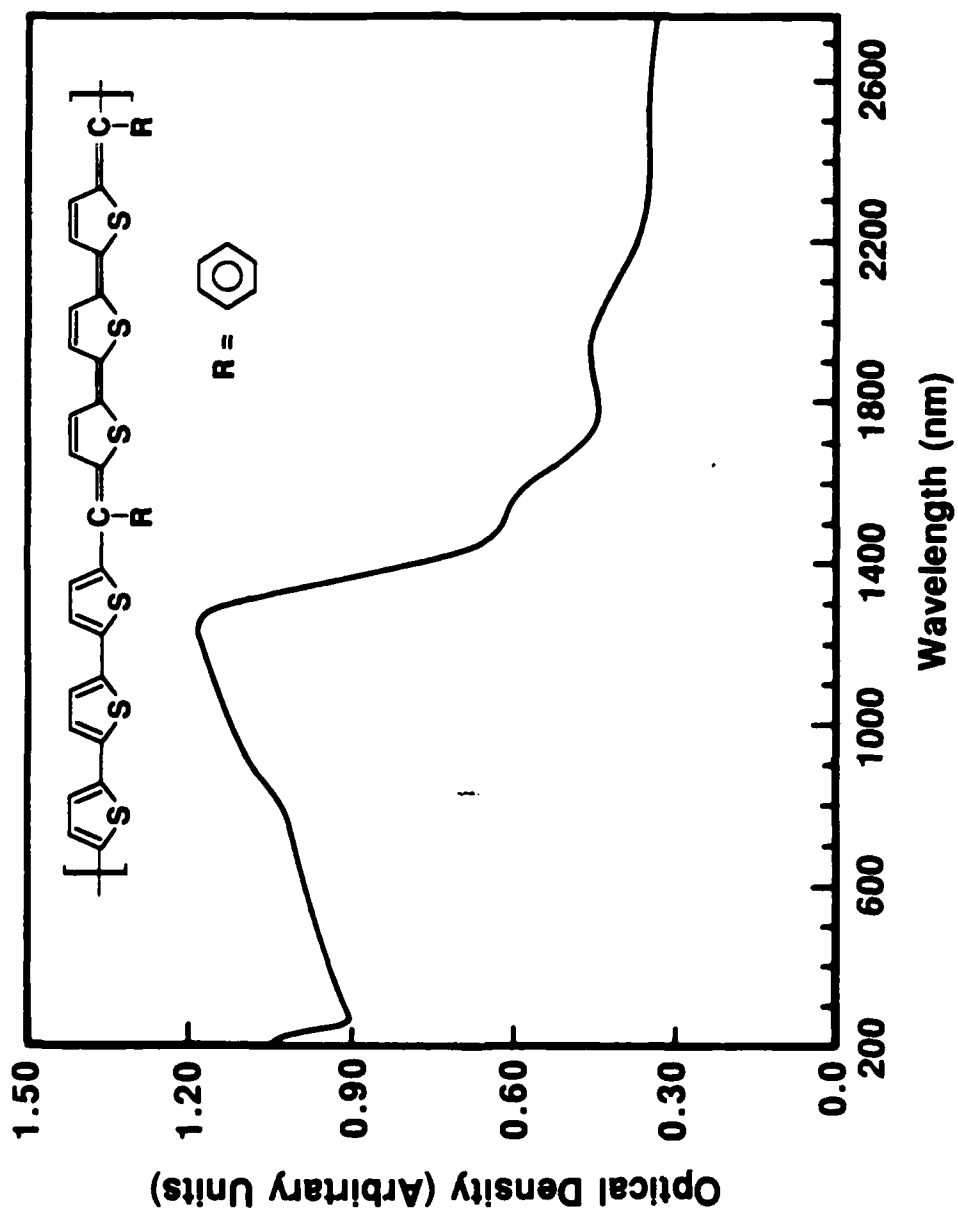


Fig. 9



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Fig. 10 A

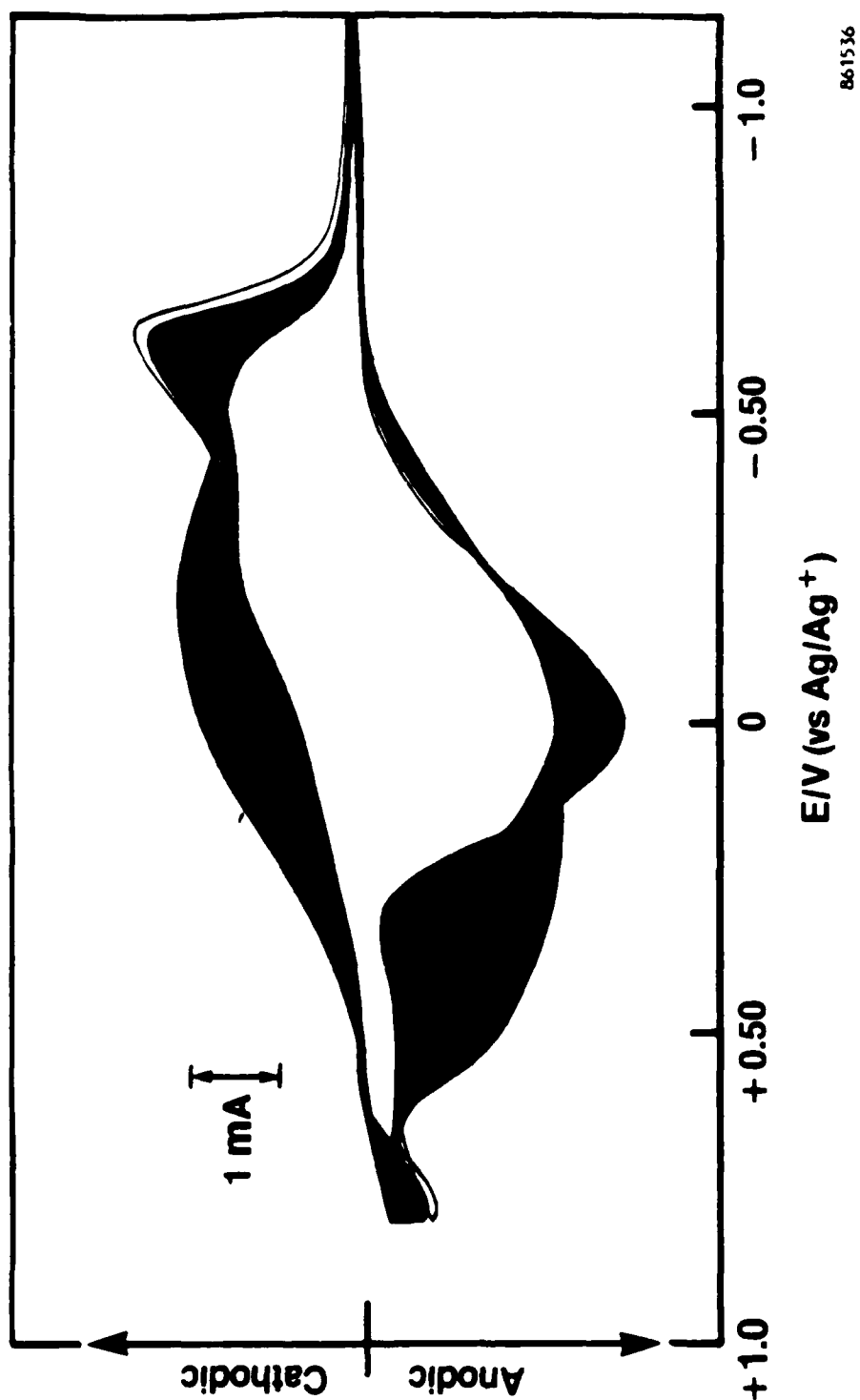


Fig. 10B

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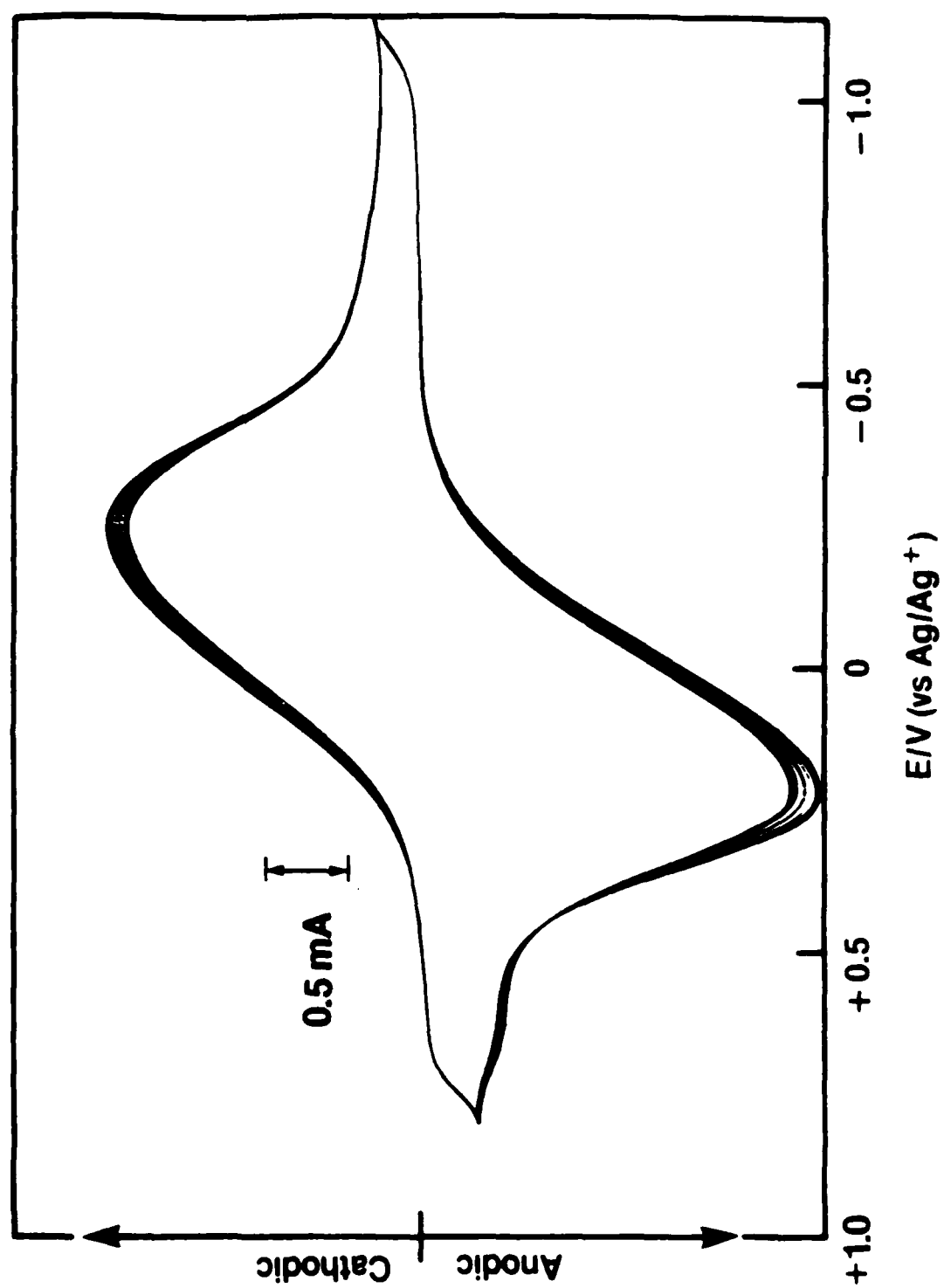


Fig. 11

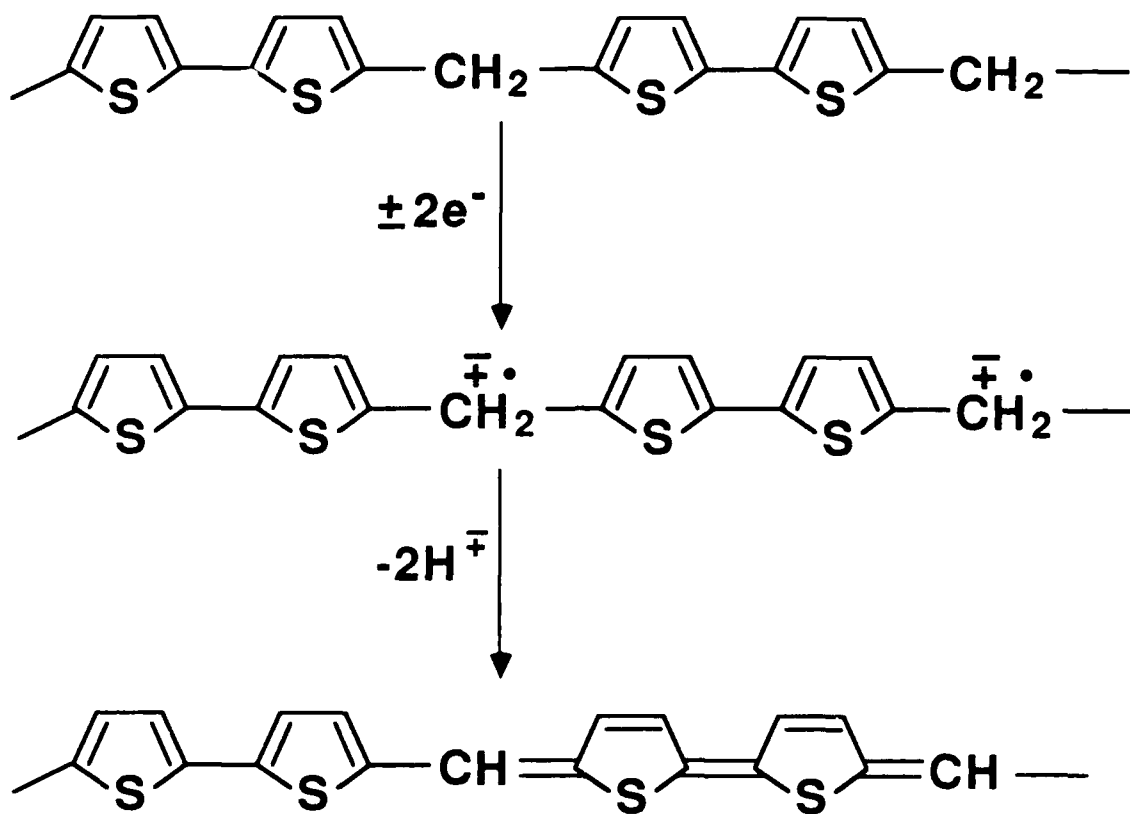
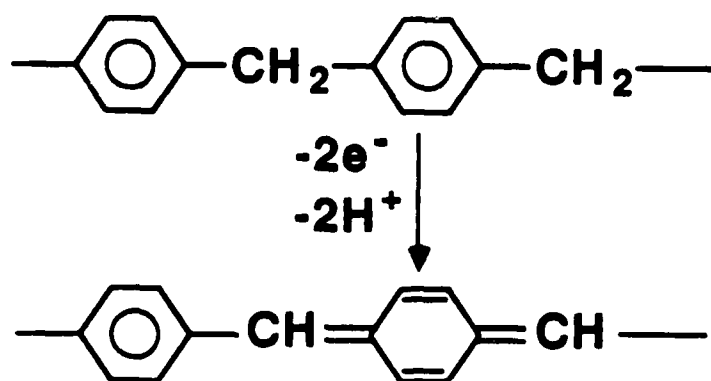
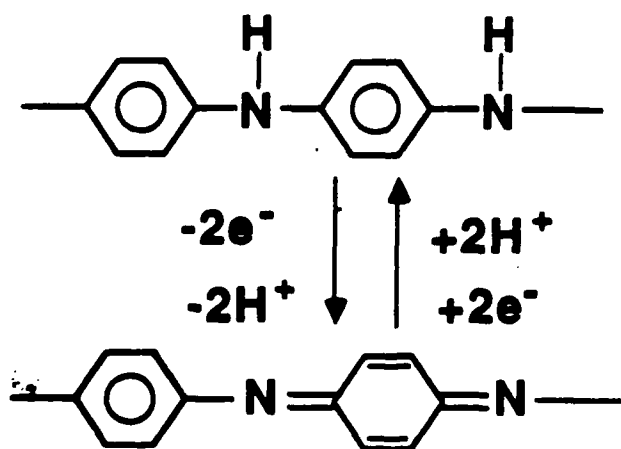


Fig. 12

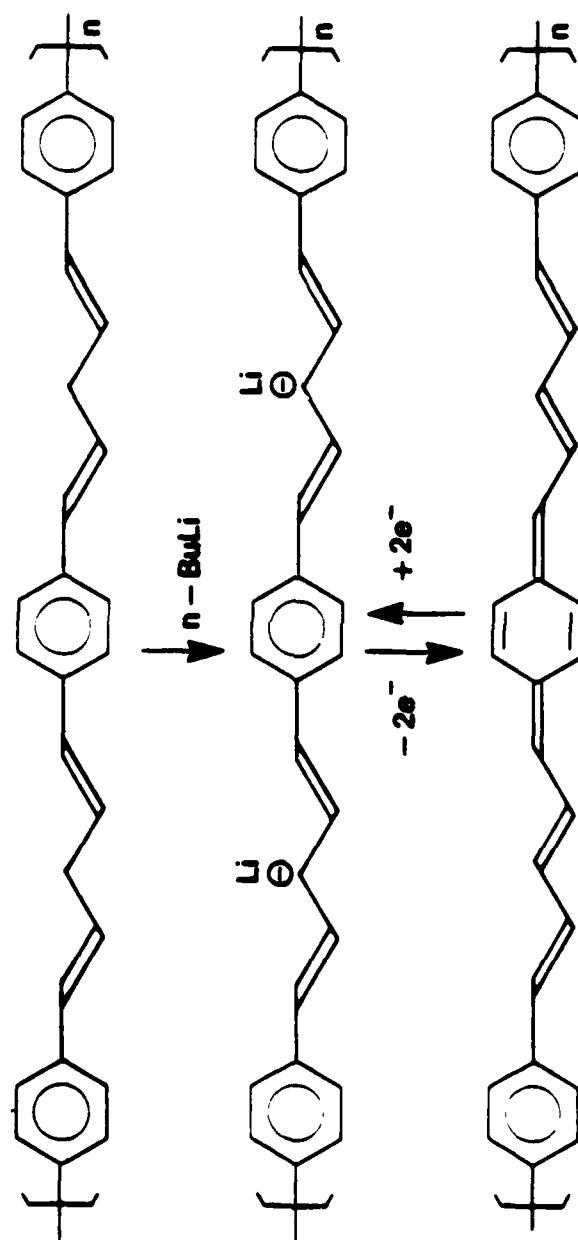


A



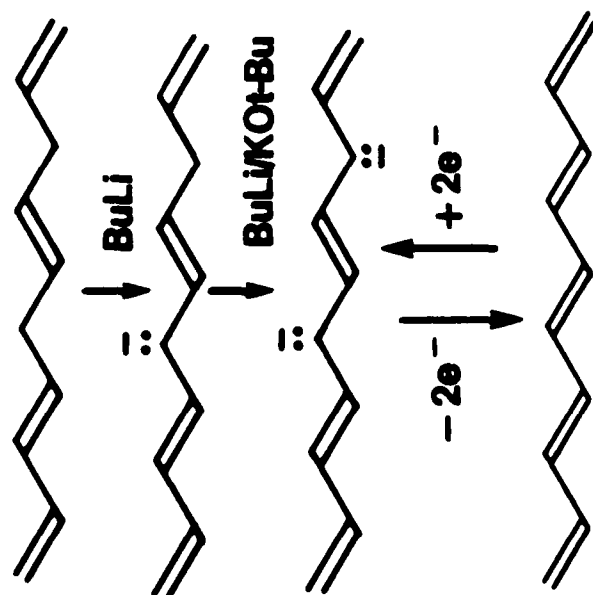
B

Fig. 13



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Fig. 14



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